

Synthesis and properties of photoreactive polysiloxanes containing pendant functional groups

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Abstract - Functional polysiloxanes containing photo-reactive pendant groups were prepared by multi-step modification of silicone copolymers containing methylhydrosiloxanes units. A first method based on the platinum catalyzed hydrosilylation of vinylsilyl terminated photoreactive esters allowed to prepare liquid silicone polymers containing photo-dimerizable esters. Another method based on the esterification of pendant epoxy groups previously grafted on the silicone main chain was found as a general and very powerful alternative route to prepare photo-reactive polysiloxanes. The method has been applied to synthesize polysiloxanes containing various functional side-groups such as dimerizable esters, aromatic carbonyl compounds or dyes which possess properties of photochemical interest.

The reactivity, the ability to be photosensitized as well as some practical properties of different photo-crosslinkable polysiloxanes modified either by cinnamic, furacrylic or α cyano β styrylacrylic ester groups were examined. A kinetic investigation of the reactivity of the polysiloxane-bound dimerizable chromophores allows to point out the effect of the silicone matrix in comparison with more classical hydrocarbon photopolymers.

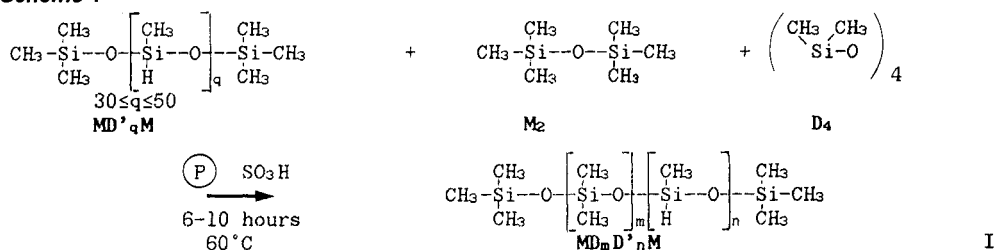
INTRODUCTION

Polysiloxanes containing pendant functional groups receive increasing interest because they possess some outstanding properties making extremely attractive their use in various applications as biomedical material (ref.1), surface-coating resins (ref.2) or liquid crystalline polymers (ref.3). Surprisingly it is almost exclusively in the patent literature or in technical papers (ref.4) that are described such silicone-based systems having additional photochemical properties allowing process in the molten state and subsequent immobilization by UV curing. We now report on the basic problem of the synthesis of well-defined photo-sensitive polysiloxanes and on the study of some of their properties.

SYNTHESIS OF PHOTO-CROSSLINKABLE POLYSILOXANES BY HYDROSILYLATION: A FIRST APPROACH

One of the most usual methods affording such modified silicones involves the one-step functionalization of presynthesized (co)polymers or prepolymers containing hydrosiloxane units, by hydrosilylation of a terminal carbon-carbon double bond which binds the low molecular weight compound to the macromolecular backbone (ref.5).

Some hydrosiloxane copolymers are commercially available starting material, but for systematic studies, these polymers are preferably tailored at will by acid catalyzed redistribution of siloxanic units as depicted in Scheme 1 (ref.6), where the homopolymer M-D'q-M affords the reactive D' units and where the cyclic oligomer D₄ affords the dimethylsiloxane comonomeric units. The molecular weight is controlled by introducing the appropriate amount of M₂ which acts as a chain regulator. When the equilibrium is reached, the solid catalyst is removed to avoid further redistribution reaction and the produced volatile oligomers are distilled off to give tailor-made copolymers I.

Scheme 1

Synthesis of polysiloxanes M-D_m-D'_n-M I by acid-catalysed redistribution. The nomenclature is the following : M = (CH₃)₃SiO_{0.5}-, D = -((CH₃)₂Si)O-, D' = -CH₃HSiO-.

The molecular characteristics M_n and Si-H content of the obtained polysiloxanes as determined by GPC (ref.7) or by chemical titration (ref.8) are in good agreement with the feeding composition of the mixture to be equilibrated. ²⁹Si MNR spectroscopy using the "Inverted Gated Decoupling" technique shows that the equilibration reaction leads to a random distribution of D and D' units in the silicone main chain (ref.9).

Table 1. Characteristics of some taylor-made polysiloxanes I.

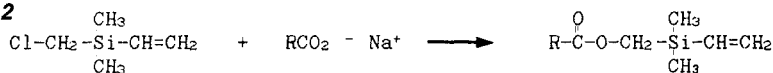
Polymer	M _n ^a	M _w GPC ^b	Si-H content (mol%)	Dynamic viscosity 25 ^c (Pa.s)
SP ₁	20,000	32,000	2	0.85
SP ₂	40,000	66,000	2	7.05
SP ₃	50,000	105,000	2	30.0
SP ₄	15,000	29,400	10	0.75
SP ₅	20,000	38,000	10	1.5
SP ₆ ⁻	30,000	56,000	10	2.5
SP ₇	15,000	34,000 ^c	20	0.4
SP ₈	17,000	36,000	25	0.5

^a Theoretical M_n based on the feeding composition.

^b Experimental average molecular weight obtained from GPC calculation based on polystyrene calibration.

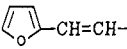
^c Polymer containing low molecular weight oligomers excluded from GPC calculations.

A first series of modification reactions to afford photo-crosslinkable polysiloxanes was performed using as starting polymers the polysiloxanes I whose characteristics are collected in Table 1. The vinyl terminated photo-sensitive esters to be grafted are synthesized by nucleophilic substitution of the chloromethyl group of the vinylsilane by the appropriate sodium carboxylate according to scheme 2 (ref.10).

Scheme 2

Synthesis of the photosensitive vinylsilyl terminated esters.

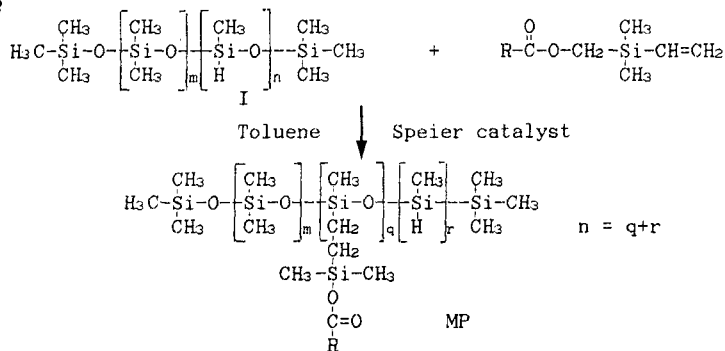
Table 2. Data of the synthesis and U.V. properties of the vinylsilyl terminated esters used.

Ester	R	Yield (%)	max () ^a
CVS	Ph-CH=CH-	84(b.p./0.1 torr: 100°)	279(22,000)
FAVS	 -CH=CH-	80(b.p./0.1 torr: 89°)	305(20,500)
CSAVS	Ph-CH=CH-CH=C(CN)-	68(m.p.: 123-125°)	347(40,000)

We have used three different esters of the cinnamic type (table 2) which are well known to dimerize to a cyclobutane derivative upon UV irradiation, by a well documented [2+2] photocyclo-addition process (ref.11). The repetition of this elementary photo-reaction along the chain of a multifunctional polymer is expected to give rise to a stepwise network formation.

The coupling reaction by hydrosilylation of the vinylsilyl end group of the esters (Scheme 3) is performed in toluene using Speier's catalyst (ref.12) as a source of platinum complex at a concentration of $1 - 5 \cdot 10^{-4}$ mol of Pt per equivalent of hydrogenosilane function.

Scheme 3



Modification of polysiloxanes I by hydrosilylation of vinylsilyl terminated esters.

Table 3. Reaction conditions and characteristics of the photosensitive polysiloxanes MP.

No	Starting Polymer	Ester	Reaction conditions			Hydrosilylation products			
			Procedure ^a	r ^b	s ^b	MP	c	d (T°)	S ^e
1	SP ₁	FAVS	a(105°)	0.95	1	MP1	2	5.1(25°)	11
2	SP ₂	FAVS	a(105°)	0.95	1	MP2	2	22.8(25°)	21
3	SP ₂	CVS	a(105°)	0.95	1	MP3	2	28.3(25°)	8
4	SP ₂	CSAVS	a(105°)	0.95	1	MP4	2	40.6(25°)	48
5	SP ₃	FAVS	a(105°)	0.95	1	MP5	2	Wax	28
6	SP ₄	FAVS	a(90°)	0.90	1.5	MP6	9	6.1(25°)	61
7	SP ₄	CVS	a(90°)	0.90	1.5	MP7	9	Wax	19
8	SP ₄	CSAVS	a(90°)	0.60	1.5	MP8	6	15.0(55°)	128
9	SP ₄	CSAVS	a(90°)	0.70	1.5	MP9	7	Wax	159
10	SP ₄	CSAVS	a(90°)	0.80	1.5	MP10	8	51.0(55°)	196
11	SP ₆	FAVS	a(90°)	0.90	1.5	MP11	9	Wax	125
12	SP ₆	CVS	a(90°)	0.90	1.5	MP12	9	Wax	38
13	SP ₅	CSAVS	a(90°)	0.50	2	MP13	5	5.1(60°)	110
14	SP ₇	CSAVS	a(70°)	0.50	3.8	MP14	10	3.8(60°)	30
15	SP ₇	CSAVS	b(6h)	0.50	4.4	MP15	10	4.1(60°)	120
16	SP ₇	CSAVS	b(9h)	0.50	5.7	MP16	10	Wax	720
17	SP ₈	CSAVS	b(7h)	0.57	2	MP17	14	11.0(60°)	420
18	SP ₈	CSAVS	b(10h)	0.57	2	MP18	14	12.8(60°)	760

^aProcedure (a) : the reaction is carried out at the indicated temperature as long as free ester is detected by TLC. Procedure (b) : the reaction is carried out at 70° (reaction time in parentheses).

^br = (free ester)₀ / (Si-H)₀ ; s = 10⁴ · (Pt catalyst) / (Si-H)₀.

^cFunctionalization rate (mol%).

^dDynamic viscosity (Pa.s).

^ePractical sensitivity determined under monochromatic light (cm²·J⁻¹).

By virtue of the high reactivity towards hydrosilylation of the vinylsilyl moiety of the three sensitive esters, acceptable reaction conditions could be found to allow the addition of the Si-H function onto the olefinic end-group with sufficient selectivity, i.e. without significant side-reactions involving the unsaturated moiety of the conjugated chromophore.

In table 3 are collected the different conditions of the reactions leading to modified polymers MP which are obtained as liquid resins when CVS or FAVS esters were grafted onto the main chain. The polymers are usually waxy at room temperature when modified by CSAVS, but recover sufficient flow-properties upon reasonable heating in the range of 50-70 °C as indicated by the results of viscosity measurements. Another quantity of practical importance is the photosensitivity S of these negative working photopolymers. The value of S, defined as the reciprocal of the minimum energy leading to the complete insolubilization of a thin film, is measured by a so-called photoresist test. The method allows to compare quantitatively the overall efficiency of the cross-linking process for linear polymers irradiated under given conditions. Depending on the nature of the sensitive ester, on the polymer chain length and on the molar content in photosensitive units, the measured values of S for this series were found to cover two order of magnitudes, the lowest value being 8

$\text{cm}^2 \cdot \text{J}^{-1}$ measured for polymer MP₃ having a low content in cinnamic group and the highest value $760 \text{ cm}^2 \cdot \text{J}^{-1}$ for a MP₁₈ having 14 mol % of CSAVS units.

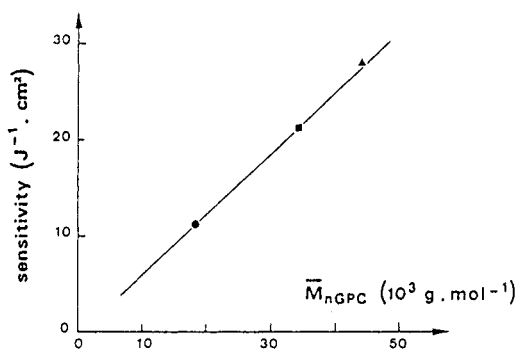


Fig. 1. Influence of the average molecular weight of the starting polymer on the sensitivity of FAVS functionalized polysiloxanes : MP1 (○), MP2 (■), MP5 (Δ). See table 3.

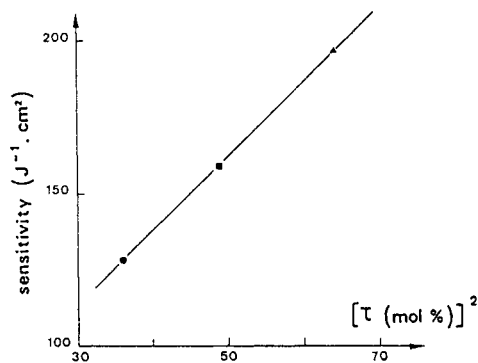


Fig. 2. Dependence of the practical sensitivity of some CSAVS functionalized polymers with the square of the molar rate in sensitive units : MP8 (○), MP9 (■), MP10 (Δ). See table 3.

From the comparison of some selected results of table 3, it is possible to point out the influence of three basic constitutional parameters on the practical photosensitivity of the modified polysiloxanes : for a fixed content in given sensitive units, the average molecular weight of the parent copolymer and for a fixed value of the chain length, the degree of functionalization with a given photo-reactive group. According to the theoretical treatment of Tsuda (ref.13) developed for hydrocarbon polymers, it was found that, for small variations of the two first parameters, the sensitivity has a linear dependence on the molecular weight (Fig.1) and on the square of the molar content in sensitive units (Fig.2).

The last basic parameter is naturally the nature of the photodimerizable ester. The comparison of the sensitograms of figure 3 obtained by photosensitivity measurements under monochromatic light shows the intrinsically more sensitive nature of cyanostyrylacrylic groups giving a maximum of sensitivity of $50 \text{ cm}^2 \cdot \text{J}^{-1}$ at the wavelength of the absorption maximum, when the value of S is only $20 \text{ cm}^2 \cdot \text{J}^{-1}$ for the furylacrylic derivative and $8 \text{ cm}^2 \cdot \text{J}^{-1}$ for the cinnamic one.

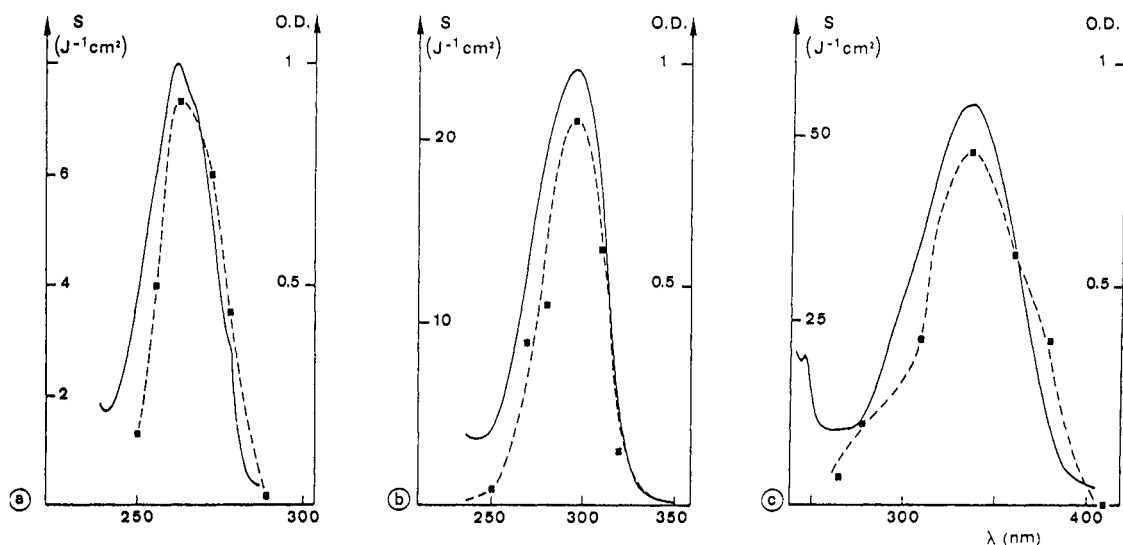


Fig. 3. Sensitograms (---) of polysiloxanes containing 2 mol % of sensitive units: MP3 (a), MP2 (b), MP4 (c) (see table 3). The corresponding UV spectra are shown by solid lines.

The improvement of the photosensitivity of this type of negative working photopolymers by the optimization of the above mentioned parameters is nevertheless limited

by the consecutive viscosity increase in the molten state as shown on the diagram of figure 4. The relation of practical importance between the polychromatic sensitivity (500 Watts - high pressure Hg source) and the dynamic viscosity of various polymers containing cyanostyrylacrylic esters shows that the more sensitive of the series has a viscosity exceeding 10 Pa.s at 60 °C, a high value which does not allow solvent-free coating applications.

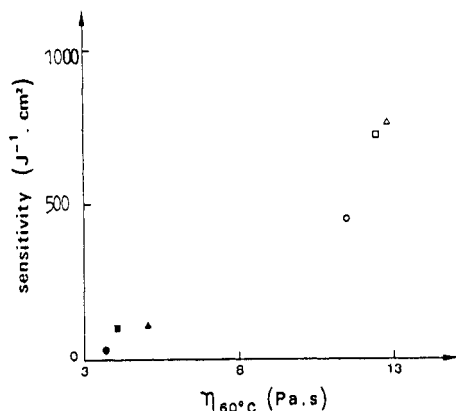
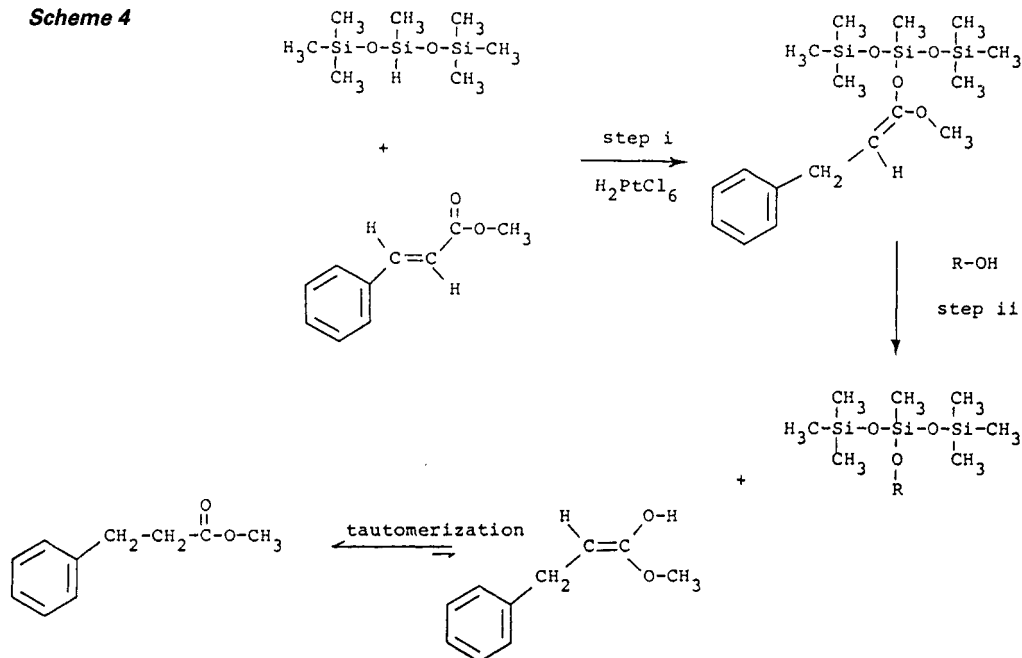


Fig. 4. Relation between the practical sensitivity under polychromatic light and the dynamic viscosity at 60°C of some CSAVS functionalized polymers : MP14 (●); MP15 (■); MP13 (▲); MP17 (○); MP16 (□); MP18 (△).

In addition to this limitation concerning the rheologic properties of the modified polymers, the functionalization reaction described in scheme 3 was found to give rise to some unwanted side-reactions involving the necessary excess of Si-H groups with respect to the sensitive ester. This problem was especially acute when the reactions were carried out with systems designed to give high values of S. The side-reactions can lead to chain branching which increases the molecular weight distribution of the polymer all along the modification as evidenced by size exclusion chromatography (ref.14) and finally induces the gelation of all the reaction mixture by chemical cross-linking. A spectroscopic evidence of one type of possible side-reaction obtained by NMR analysis of some polymers modified by cinnamic esters CVS clearly indicated (ref.10) that the hydrogenation of the double bond of the chromophore can take place to some significant extent. The study of a model reaction indeed gave confirmation of the formation of dihydrocinnamic esters in the presence of Si-H, as depicted in scheme which involves at first a 1,4-hydrosilylation process followed by hydrolysis or alcoholysis of the silyl enoether.

Scheme 4



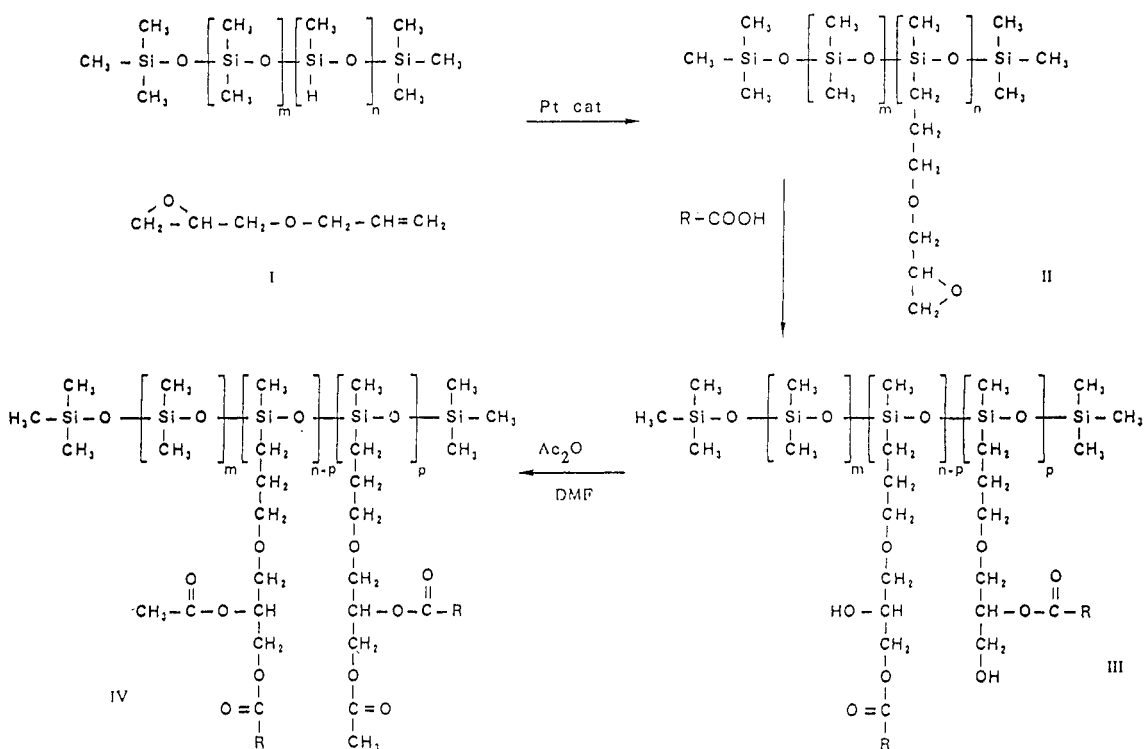
Mechanism of the hydrogenation of the cinnamic chromophore in the presence of hydrosilane functions.

These various problems due to ill-controlled processes, together with the cost of preparation of the vinylsilyl terminated esters, prompted us to search for a general method of synthesis of multifunctional liquid polysiloxanes in which the necessary hydrosilylation step would be performed with an olefin of low functionality in order to avoid such side-reactions.

SYNTHESIS OF PHOTOREACTIVE POLYSILOXANES BY ESTERIFICATION OF PENDANT GLYCIDIC GROUPS

The catalyzed addition of a functional carboxylic acid on a pendant epoxy group to give a β -hydroxy ester appears as a versatile key-step (ref.15) to be introduced in the reaction sequence of scheme 5. According to this method, tailor-made copolymers I are modified in a first step by hydrosilylation of allyl glycidyl ether to give with quantitative conversion and high selectivity polymers of type II. In a second step, the addition of a carboxylic acid is performed to afford the expected hydroxyester pendant groups observed in polymers III as a mixture of the two position isomers.

Scheme 5



Functionalization of polysiloxanes by esterification of pendant glycidic groups.

We have studied the main esterification feature of the pendant glycidic groups by model carboxylic acids either in the presence of a tertiary amine as a catalyst in low polarity media (ref.16) or with tetrabutylammonium bromide as a catalyst for reactions carried in polar aprotic solvent (ref.17). No important problem of chemical selectivity could be observed during the course of the epoxy-carboxy reaction, but the recovered polymers of type III were obtained in most cases as untractable gummy products hardly soluble after standard purification workup. This phenomenon which was shown to only result from physical associations between the chains by intermolecular hydrogen bonding, was finally avoided by the ultimate acetylation of polymers III to give liquid or waxy polysiloxanes IV whatever the length of the chain or the content in functional pendant groups.

This novel method was used to prepare a variety of multifunctional liquid polysiloxanes among which photosensitive polymers of type III or IV with cinnamic (CIN) or cyanostyrylacrylic (CSA) pendant ester groups (ref.18) were studied in some details. The values of the practical sensitivity (S), determined by insolubilization tests, are collected in Table 4. The comparison of the results obtained with the two series of polymers III and IV indicates that the acetylation reaction has only little influence on the practical sensitivity of polymers containing ester groups deriving from VIa. A somewhat more significant loss is

observed when the acetylated polymer IVg with a short silicone chain or IVc containing cinnamic ester groups of lower polarity has a low viscosity as a consequence of weaker intermolecular interactions. The insolubilization of the network, therefore, requires a more important number of covalent cross-links leading to a lowered value of the practical sensitivity, as measured for the two acetylated polymers. The intrinsically more sensitive nature of the ester deriving from CSA appears from the comparison of the values of S obtained with polymers IIIb (or IVb) with regard to IIIc (or IVc), the latter being about ten times less sensitive. The degree of polymerization DP_n of the functionalized polymers has a prime effect on their practical sensitivity, while the functionalization polymers rate seems to be of secondary importance in the range of DP_n covered by the studied samples.

Table 4. Results of practical sensitivity and dynamic viscosity measurements on photosensitive polymers of type III and IV.

Polymer of type III	S^a cm^2J^{-1}	Polymer of type IV	S cm^2J^{-1}	DP_n^b	Sensitive ester	Content ^c in mol%
a	450	a	435	401	CSA	4.1
b	250	b	240	241	CSA	5.8
c	23	c	18	241	CIN	6.5
d	200	d	-	251	CSA	10 ^d
e	155	e	140	209	CSA	7.5
f	100	f	90	129	CSA	9.5
g	50	g	40	33	CSA	14.2

- a) Practical sensitivity determined by photoresist tests under monochromatic light $\lambda = 345$ nm, except for polymers IIIc and IVc ($\lambda = 280$ nm).
 b) Deduced from GPC measurements performed with the parent polymers 2.
 c) Deduced from UV absorbance measurements.
 d) Not measured. Theoretical maximum value.

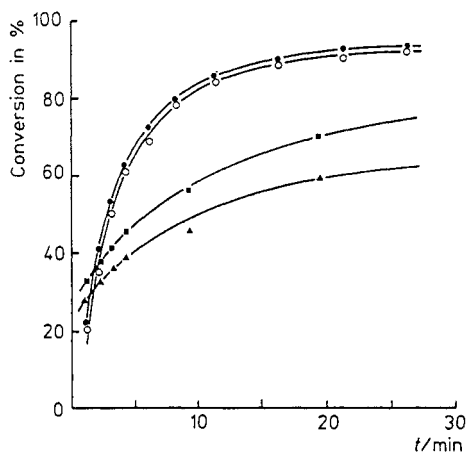


Fig. 5. Disappearance (deduced from UV absorption measurements) of the photosensitive groups in polysiloxanes III or IV upon irradiation with 280 nm UV light ($I = 220 \cdot 10^{-6}$ W.cm⁻²). IIIb (\blacktriangle), IVb (\blacksquare), with 345 nm light ($I = 230 \cdot 10^{-6}$ W.cm⁻²) IIIg (\circ), IVg (\bullet).

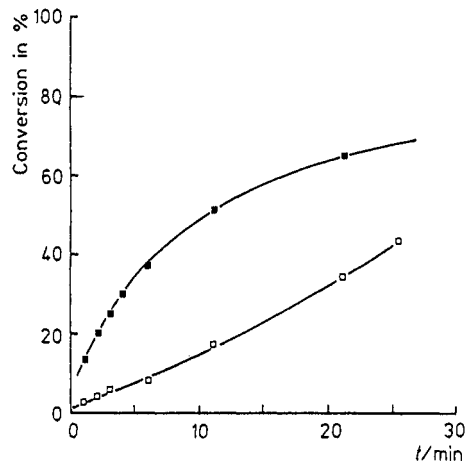


Fig. 6. Disappearance (deduced from UV absorption measurements) of the photosensitive groups in acetylated polymer IVb (\blacksquare) upon irradiation with 345 nm UV light ($I = 230 \cdot 10^{-6}$ W.cm⁻²) and (\square) immediately after short heating at 60-70°C.

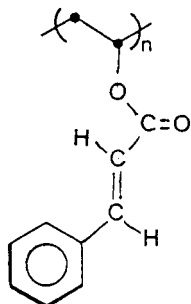
The plots of Fig. 5 and 6 show the variations of conversion against the irradiation time for plates coated with polymers III or IV (initial optical density in the range 1.7 - 2). The experimental conditions of these first semi-quantitative measurements do not allow a detailed kinetic analysis of the process but the following comments have to be pointed out. The comparison of the conversion vs time curves obtained with polymers IIIg and IVg, and on the other hand IIIb and IVb (Fig. 5) indicates that the acetylation reaction has only little influence on the conversion rate of polymers modified with CSA esters when, in apparent contradiction with the results obtained from practical sensitivity measurements (insolubilization tests), the rate was shown to be increased for the cinnamic derivative. This phenomenon has to be connected with the increase in mobility favourable to the bimolecular photo-chemical reaction (ref.19).

The change in the conversion curve of polymer IVb irradiated after annealing but without chemical degradation of the sample (bottom curve of Fig. 6) suggest on the contrary, that the polysiloxanes containing cyanostyrylacrylyc esters possess a certain degree of organization inducing a higher reactivity but are sensitive to the thermal history of the sample. The influence of the physical state of the polymeric material on the reactivity is exemplified in the next section.

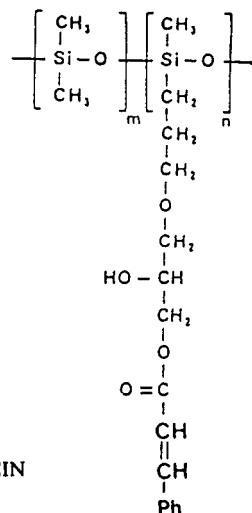
REACTIVITY OF POLYSILOXANE WITH PENDANT PHOTODIMERIZABLE ESTER GROUPS

Polymers with pendant cinnamic esters

The photoreactivity of polyvinylcinnamate (PVCi) or related hydrocarbon systems has been studied by Reiser (ref.20). The addition of the pendant groups is the almost single reaction occurring in the solid matrix when films of the polymer are exposed to UV light in the glassy state. A typical limit value for the overall conversion lies in the range of 50 mol%. Even when PVCi is irradiated in dilute solution, the dimerization - oligomerization is still the main process despite the low concentration, the deactivation of excited chromophores by reversible cis trans isomerization of the conjugated olefin competing only to a slightly lower extent.



PVCi



Polymer of type III CIN

In dilute solutions, with initial concentration in cinnamic ester in the range of 50 $\mu\text{mol.l}^{-1}$, polysiloxanes of type III or IV showed reversible E-Z isomerization as observed on the UV spectra showing an isobestic point. The absence of addition reaction between the cinnamic groups contrasting with the behaviour of PVCi is due to the length of the spacer connecting the sensitive moiety to the highly flexible main chain. When examining the photoreactivity of neat films of the sensitive polymers, it is possible to follow by UV spectroscopy at the two wavelength corresponding to the maximum of absorption of the pure E chromophore (279 nm) and to the isobestic point of the isomerization respectively (249 nm), the variations of the mol ratio of the different species, E and Z forms of the cinnamate and of the dimers. For very thin films giving an initial optical density below 0.1, the photochemical excitation is homogeneous (no significant gradient of light intensity depending on the depth of the film) and the variations of species are totally representative of the overall process. The curves of Fig. 7, obtained from a series of three polymers of type III, show that the main reaction taking place during the very first moments of the irradiation is the isomerization of the pure E cinnamate to give rapidly a mixture of the two isomers in dynamic equilibrium. The dimerization starts but much more slowly, accounting for a collision controlled process totally different from the topochemical control by the crystal lattice of the dimerization of cinnamic acid (ref.21) or from the reaction in the glassy matrix of PVCi. Indeed, the initial absolute rate of the dimerization roughly correlates with the weight content in photosensitive group. The comparison between the limit values of the dimerization - oligomerization process would not be relevant in the present case, since the three polymers have very different DPn. The formation of the network which reduces the mobility of the reactive groups during the course of the dimerization is strongly dependent on this macromolecular parameter and has naturally a determinant influence on the plateau value.

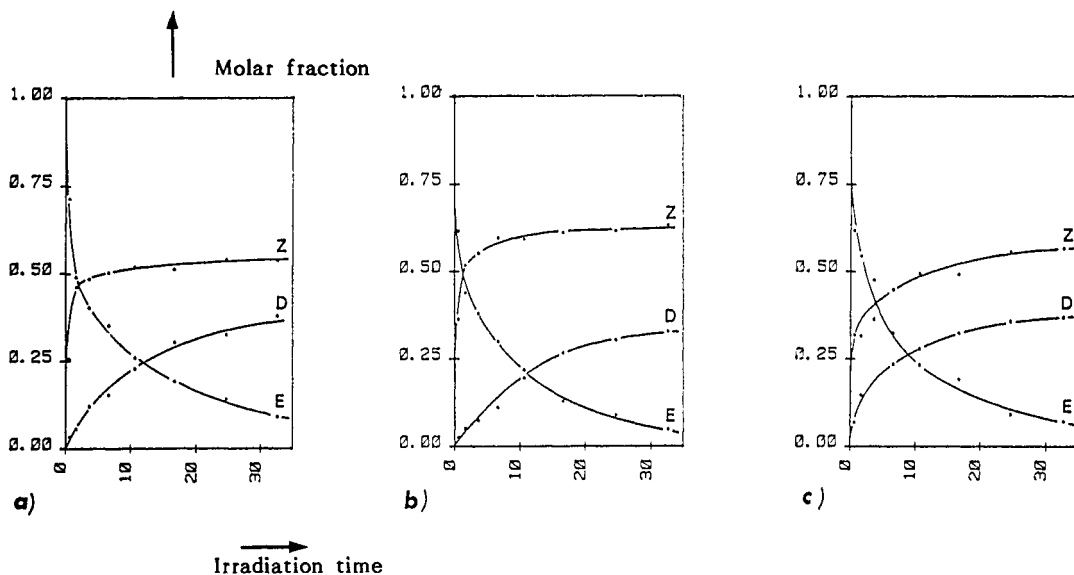


Fig. 7. Conversion vs time plots of cinnamic esters in neat films of polysiloxanes of type III with 25 (a), 44 (b) and 100 mol % (c) of pendant cinnamic groups under the light of a 900 Watts Xenon source.

Polymers with pendant CSA esters

UV light irradiation of dilute solutions ($C < 5 \cdot 10^{-5}$ M) of free CSA esters or of copolymers containing CSA pendant groups leads to a change in their UV spectra with persistence of an isobestic point at 304 nm attributed to the isomerization of the chromophore. When irradiated under similar conditions, neat films of sensitive polysiloxanes MP (See Table 3) or of type III or IV - whatever the nature of the spacer linking the CSA ester to the chain - gave UV spectra with an isobestic point at a shorter wavelength (288 nm) as shown on Fig.8a.

CSA esters thus show two very clean-cut types of behaviour : in solution one observes only a monomolecular isomerization attributable process when, in neat polymeric samples, takes place a single different process to the dimerization to give well-defined cyclobutane products. The retro-dimerization known to be photo-activated by 255 nm light irradiation of crystalline model esters (ref.22) is indeed observed, as shown on Fig. 8b. The reversibility is high if the conversion into the dimer has been limited to a value below 50%. In the case presented in Fig. 8b the recovered optical density at 345 nm, more than 80% of the initial value accounts for a good selectivity suggestive of a matrix controlled reaction (ref.23). Further work is currently in progress to correlate kinetic parameters of the dimerization process with the micromorphology of these systems. It is likely that the polar nature of the photosensitive ester induces phase separation of domains having a partially ordered structures.

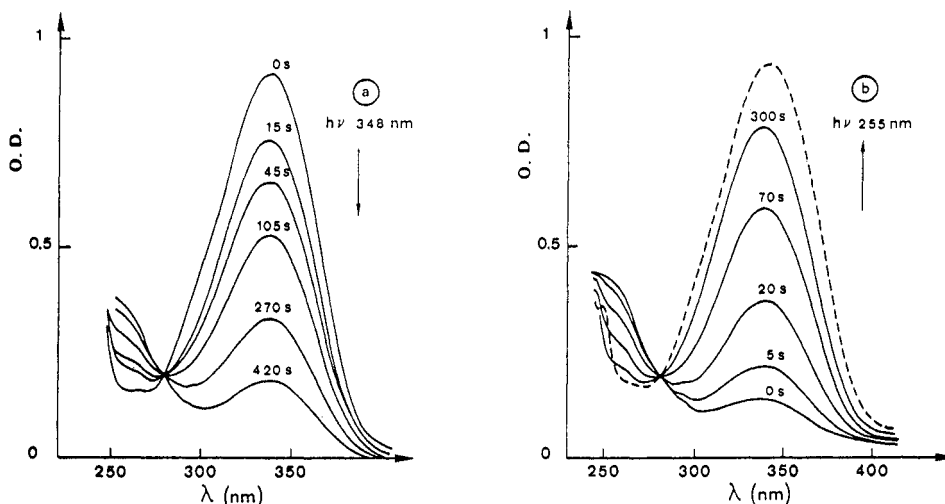


Fig. 8. (a) Changes in the U.V. spectra of MP8 upon 348 nm irradiation ; (b) reversibility of the [2+2] photo-cycloaddition reaction by 255 nm irradiation of the crosslinked polymers.

Photosensitization of the cross-linking process

For many applications as negative photoresists, hydrocarbon polymers crosslinkable by a [2+2] cyclo-addition process are used with photosensitizers in order to give a better overlap between industrial light sources and the spectral response of the whole formulation (ref.24). We have used typical triplet sensitizers as the different phenones mentioned in the legend of Fig. 9 and some other compounds to enhance the reactivity of cinnamic polysiloxanes. A clear effect of spectral sensitization is observed with these systems despite the heterogeneous nature of the mixture. The efficiency is naturally extremely poor with polymers of low rate of functionalization (2 - 20 mol%) in reason of the low concentration in reactive groups which dramatically affects the probability of encounter of a pair of esters with the excited sensitizer. The influence of the nature of the photosensitizer clearly appears from the comparison of the curves obtained with a polysiloxane of type III containing 44 mol% of cinnamic groups. The results confirm the good efficiency of MK and BN (ref.24) which give with a filtered incident light a rate of disappearance of the cinnamic esters in the same range than for the direct excitation of the chromophore using the whole emitted spectrum of the light source.

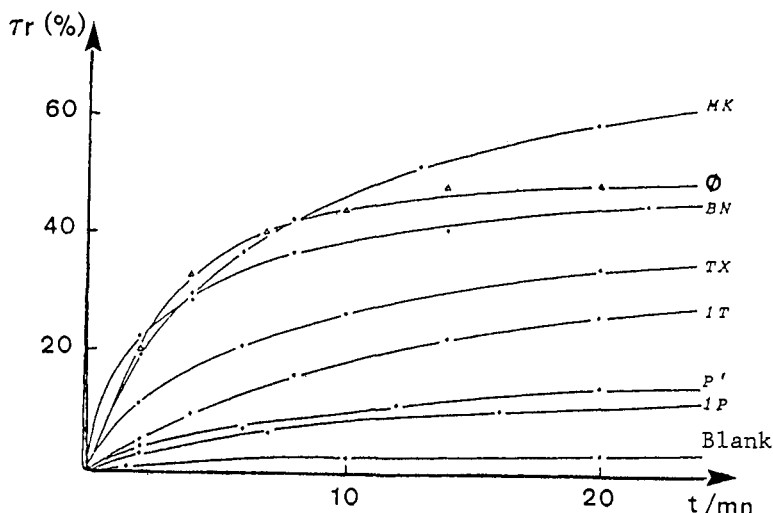


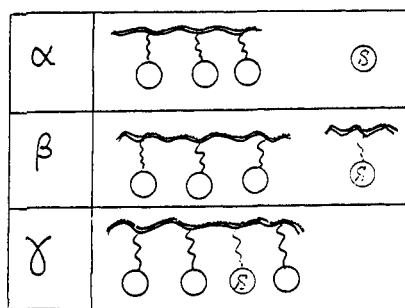
Fig. 9. Variations of the conversion rate of a polysiloxane of type III with 44% molar of photosensitive cinnamic ester units, in the presence of various photosensitizers (5 wt %). Φ is the curve obtained when the 900 Watt Xenon lamp is used without light filter. The other curves were obtained with incident light of wavelength $\lambda > 320$ nm. BP = Benzophenone, BN \square N-methyl 2-benzoylmethylenenaphthothiazoline, MK \square Michler's ketone, P = pyrene, TX = thioxanthone, 1P = 2,4,6-triphenyl-2,4,6 pyrylium perchlorate, IT = 2,4,6-triphenyl-thiapyrylium perchlorate.

The sensitization of polysiloxane with pendant CSA groups by different pyrylium salts has also been tested. The photocross-linking then proceeds with loss of the isobestic point in the UV spectra recorded during the course of the irradiation. Pyrylium salts which are known to give rise to electron transfer, presumably induce additional radical processes leading to the addition of the double bonds (ref.25). Practical photoresist tests show anyway that the sensitized compositions are about 3 times more sensitive than the pure polymer under the polychromatic light of a Xenon lamp.

To examine if the increase in practical sensitivity by spectral sensitizers could be enhanced by inducing a better compatibility between the functional polysiloxane and the added compound we have prepared, using the different synthetic methods described in this paper, the sensitizing systems shown in scheme 6.

- a) BP or 1P added in bulk
- β) vinyl derivative of BP or carboxylic derivative of 1P fixed on an oligomeric siloxane
- γ) vinyl derivative of BP or carboxylic derivative of 1P fixed on the polysiloxane chain as comonomeric unit.(3P)

Scheme 6



Different modes of sensitization.

The curves of Fig. 10 allow to compare the rate of disappearance of the cinnamic esters of a polymer of type III show that the initial slope in systems γ) is steeper than with modes of sensitization α) and β) which give in turn very similar results whatever the type of sensitizer, aromatic carbonyl BP or pyrylium salt 1P. Increases in practical sensitivity with factors in the range from 4 to 11 could be measured with such systems.

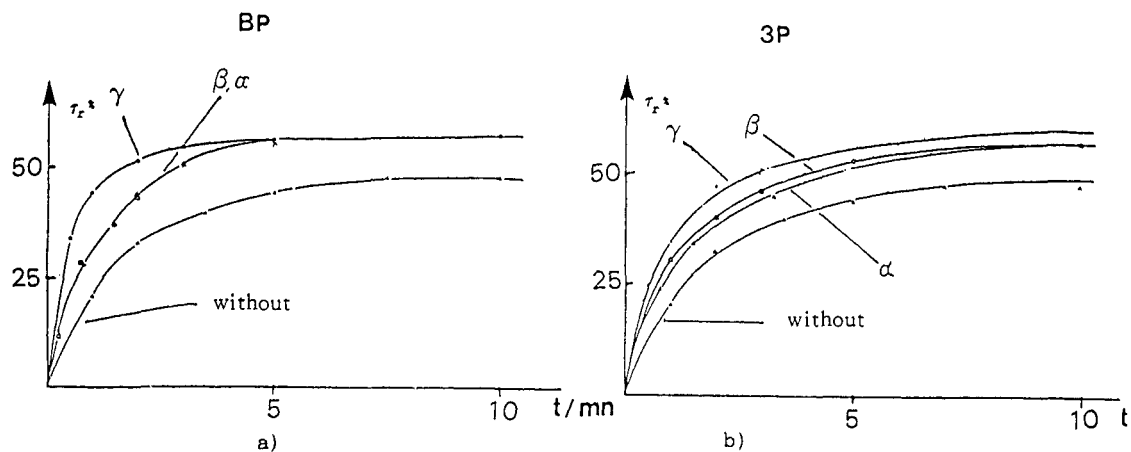


Fig. 10. Variations of the conversion rate of polysiloxane III with pendant cinnamic groups (44 mol%) sensitized by benzophenone (a) or pyrylium salt derivatives (b) in various manners, the percentage of sensitizer being constant (5 wt %) under the polychromatic light of a 900 Watts Xenon lamp.

CONCLUSION

We have described a general method for functionalisation of polysiloxanes which allowed us to prepare a variety of liquid photocrosslinkable resins. Some of the properties of these materials have been examined with a view to their practical application. A more basic study based on kinetic measurements points out some special features of photodimerisation of polysiloxane-bound chromophores. Other applications of photochemical interest have been developed. Multifunctional polysiloxanes with pendant acrylic groups have been used as source of radically polymerisable monomer in UV-curable resins. Grafting on silicone chains mesogenic side-groups together with dyes and photocrosslinkable esters affords novel material for non linear optics (ref.26). Finally, macromolecular but liquid photo-initiators of the polymerisation of acrylic monomers have been prepared by grafting aromatic carbonyl compounds onto silicone main chains. The study of the photochemical processes occurring with these efficient systems in the presence of amino compounds are currently in progress.

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